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(Australian Petty Patent)

(54) Title

AN IMPROVED ELECTROCHEMICAL MEMBRANE FILM OR FIBRE

(51)<sup>5</sup> International Patent Classification(s)  
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(56) Prior Art Documents

EP 459657

EP 442605

GB 2150598

(57) The present invention relates to the production of a flexible polymeric film or membrane based upon a polyurethane resin or polymer as the continuous phase and containing interpenetrating or semi-interpenetrating polymers with electrical conductivity and/or ion exchange properties such that the final film or membrane exhibits ionic conductivity, electrical conductivity, or both ionic and electrical conductivity. The polymeric film may additionally contain carbon, metal, metal salts, metal oxides all included as a powder, and/or carbon fibres, metal coated carbon fibres or metallic threads or wires. The fibres, threads or wires may be present in a number of different forms as disclosed within this specification.

By using the film or membrane in a cell designed to enable electrical potentials to be applied to it the polymer can promote the transport of metal ions through or into the membrane thereby enabling their recovery from solution. Alternatively, the electrically conducting film can recover metal ions from solution and also elute these recovered metal ions, the ion exchange properties being controlled by application of an electrode potential between the polymeric material and a counter electrode.

#### CLAIMS

1. A polymeric membrane or film produced from a polyurethane resin containing both poly(propylene oxide) and poly(ethylene oxide) units as the continuous phase and containing one or more interpenetrating or semi-interpenetrating polymers with electrical conductivity and/or ion exchange properties or capable of chemical modification to provide electrical conductivity or ion exchange properties such that the final film or membrane exhibits ionic conductivity, electrical conductivity, or both ionic and electrical conductivity.

AUSTRALIA

Patents Act 1952

PETTY PATENT SPECIFICATION.

Application Number: 19331/92.

Lodged: 1/7/1992.

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Petty Patent Specification for the invention entitled:

"AN IMPROVED ELECTROCHEMICAL MEMBRANE FILM."

The following statement is a full description of this  
invention including the best method of performing it known to  
me:-

The present invention relates to the production of a flexible polymeric film or membrane based upon a polyurethane resin or polymer as the continuous phase and containing interpenetrating or semi-interpenetrating polymers with electrical conductivity and/or ion exchange properties such that the final film or membrane exhibits ionic conductivity, electrical conductivity, or both ionic and electrical conductivity. The polymeric film may additionally contain carbon, metal, metal salts, metal oxides all included as a powder, and/or carbon fibres, metal coated carbon fibres or metallic threads or wires. The fibres, threads or wires may be present in a number of different forms as disclosed within this specification.

By using the film or membrane in a cell designed to enable electrical potentials to be applied to it the polymer can promote the transport of metal ions through or into the membrane thereby enabling their recovery from solution. Alternatively, the electrically conducting film can recover metal ions from solution and also elute these recovered metal ions, the ion exchange properties being controlled by application of an electrode potential between the polymeric material and a counter electrode.

The present invention may be used for applications such as recovery of precious metals from solution; the removal of toxic or heavy metals from wastewater streams; removal of corrosive anions, water deionisation, concentration of metal ions within an electrochemical cell, etc. The invention is not limited to the above applications, but can be also applied to other aqueous streams for removal of other cations, anions, radionuclides etc. The membrane or film can also be applied as a separating membrane in redox battery technology by preventing the anolyte and the catholyte from mixing whilst still allowing transport of the conducting ions thereby completing the circuit during the passage of current. These films could also be applied to the conductance of an electrical current to heat a surface such as in deicing applications, etc.

In traditional metals recovery technology, recovery or removal of metal ions from aqueous solution is accomplished by cementation processes, precipitation following pH control, activated carbon sorption, ion exchange, solvent extraction or other known technology including the use of membranes, dialysis etc.

Electrochemical ion exchange (EIX) has been proposed by Bridger, Jones & Neville, Electrochemical Ion Exchange, J. Chem. Tech. Biotechnol. (1991), 50, 469-481 and various designs of this technology are disclosed by Bridger and Turner in UK Patent Application 2 150 598 A dated 3 July 1985 and in European Patent Application 0 442 605 A1 dated 11 January 1991. They favourably compared the performance of their cell with electrodialysis and also electrodialysis combined with conventional exchange for the removal of cations and anions from aqueous solution.

The cell proposed by Bridger, et al. was manufactured by grinding commercial ion exchange materials to a fine powder of mean particle size approximately 0.1 mm then mixing this with a synthetic rubber binder dissolved in a solvent, pouring the binder solution into a mould containing platinised titanium mesh electrodes and allowing the solvent to evaporate. The kinetics of loading of metal ions are reduced because of the relatively low surface area of the ion exchange beads thereby providing a limited number of active ligands for ion exchange. The rubber binder also further restricts the rate of transport of metal ions through the membrane.

This membrane improves the performance of Bridger's electrode by significantly improving the physical and chemical properties of the membrane and by increasing the available number of active sites within the membrane. The method of production of the membrane described herein enables the ion exchange material to be more uniformly dispersed throughout the polyurethane polymer. The metal ions are therefore able to more rapidly contact the aqueous phase thereby improving the kinetics for removal of these ions from solution. The membrane described herein may also be applied in other cell designs including redox batteries, and in conventional membrane separation technology.

Polyurethane resins are employed to produce the continuous phase of the polymeric film. The interpenetrating or semi-interpenetrating phase consists of acid based cation exchangers and/or basic anion exchangers together with one or more electrically conductive polymers. Interpenetrating and semi-interpenetrating polymers are fully described in Volume 8 of Encyclopedia of Polymer Science and Engineering, published by John Wiley & Sons, New York, in the Chapter entitled "Interpenetrating polymer networks" commencing on page 279.

Elastomeric polyurethanes offer excellent flexibility over a wide range of temperature conditions. The polyurethane resin may be produced from polyester or polyether resins, with polyether resins favoured due to their improved chemical resistance. Poly(propylene oxide), or mixtures of both poly(ethylene oxide) and poly(propylene oxide) may be used in the production of the polyether based polyol. Polyols containing poly(ethylene oxide) provide improved hydrophilicity over poly(propylene oxide) based polyols and the presence of poly(ethylene oxide) in the polymer structure is important. The post-incorporation of other known chemicals such as polyethylene glycol can be used to further modify the hydrophilic properties of the base polyurethane polymer. Also, the metal ion extraction properties of the film may be further modified by post-incorporation of chemicals which are well known to provide solvent extraction properties in hydrometallurgical separation processes and these would include acid extractants, basic extractants, neutral or solvating extractants, chelation extractants and ion-pair extractants.

Ion exchange resins incorporated into the polymer may be based on organic resins such as for instance polystyrene-divinylbenzene resins containing carboxylate groups, or inorganic ion exchangers such as zirconium phosphate, or secondary, tertiary or quaternary ammonium moieties, etc.

These resins may be incorporated into the membrane by soaking the polyurethane film either separately in each monomer or in a mixture of two monomers capable of undergoing crosslinking such as for example styrene monomer and divinyl benzene monomer. Preferably, both monomers should be pre-mixed into a solvent such as methanol. Polymerisation is then achieved using a suitable polymerisation catalyst under conditions known to be favourable for polymerisation. Further ligands may then be attached to the polystyrene by the well-known chloromethylation reaction followed by conventional ligand chemistry. Other ion exchange resins may be incorporated by a similar technique of dispersion of the reactants into a solvent, soaking the film in the reactant solution for a sufficient period of time, then polymerising the reactants using a suitable catalyst and at temperatures and pressures favourable for the polymerisation reaction to proceed.

In a similar manner, electrical conductivity is achieved by throughout the polymer by incorporation into the membrane film an electrically conducting polymer such as polyaniline, polyacetylene, polypyrrole, etc. For example, polypyrrole may be produced within the membrane by soaking the film in a solvent such as acetonitrile containing ferric chloride and pyrrole monomer and providing sufficient time for curing to occur. Alternatively, the membrane may be presoaked in a pyrrole monomer-solvent solution and the monomer polymerised electrochemically. Sodium p-toluene sulphonate may be incorporated in the monomer solution to provide an increase in molecular anisotropy and polymerisation obtained by electrochemical methods. Additionally, anions such as chlorides may be incorporated during the polypyrrole synthesis to produce anion exchange materials. This process is not limited to these particular mechanisms of providing electrical conductivity.

Carbon, metals, metal salts or metal oxides, preferably in powder form, may also be incorporated into the polyurethane resin during its manufacture.

Electrically conductive fibres may also be incorporated into the elastomeric film or membrane. For instance carbon fibre may be incorporated as a woven matt, a continuous fibre or as a chopped strand matt. The carbon fibre may be coated with a metal such as gold, nickel, copper, platinum, etc by electroplating or other known deposition processes. Metallic threads, wires, or strips may also be incorporated into the membrane. Suitable electrically conductive metals or alloys would include copper, aluminium, nickel, gold, platinum, palladium, alloys of these or other metals or any other metal or alloy considered to have suitable physical, chemical and electrical properties for the particular application.

One aim of the present invention is to provide an improved process for the removal of anions and/or cations from aqueous solution in which the exchange process is controlled electrochemically and therefore eliminates the use of chemicals to regenerate the ion exchange resin. Furthermore, it is possible to elute the recovered metal ion in a single bed-volume thus achieving a large volume reduction of eluent.

A membrane prepared by immersing a poly(ethylene oxide) based polyurethane film in an aqueous solution containing pyrrole and the sodium salt of p-toluenesulphonic acid and electrochemically polymerised was used in a three-electrode cell. Application of a known potential to an aqueous copper(II) species in the source cell to be transported through the membrane. A significant increase in the permeability of copper across the membrane was recorded.

The electrically conducting polymer containing the ion exchange sites provides a large surface area to enhance the rate of uptake or selective transport of the ion from the aqueous solution. This substantial increase in surface area allows the overall size of the process equipment to be decreased thereby reducing the cost of the recovery equipment.

The ability to use a range of inorganic and/or organic ion exchange materials makes it is possible to achieve a degree of selectivity.

Application of an electrical potential across the cell encourages the migration of ions within the cell; anions migrating to the anode, and cations to the cathode. This movement of ions enhances both the sorption and elution processes involved in removal of the ions from solution. For instance, in the removal of metal ions from solution the electrode is made to be the cathode during the sorption operation and the anode during the elution step.

During the sorption reaction the active group, typically a carboxylic acid group is deprotonated to give an overall negative charge:



where R represents the backbone of the ion exchange resin.

In order to maintain a charge balance, a cation, M' is absorbed

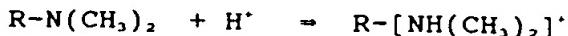


Elution is accomplished by the reprotonation of the active group:



The corresponding anion exchange reactions could involve protonation and deprotonation of secondary or tertiary ammonium groups on the resin such as,

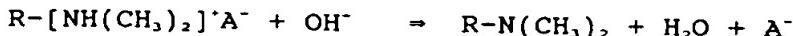
**Activation:**



**Sorption:**



**Elution:**



When the ion-exchange electrode is absorbing, the hydroxide ions produced deprotonate the carboxylic acid groups in the ion exchange resin contained in the film or fibre. For current to flow, cations are transported through the matrix to occupy vacant sites. Similarly, migration also occurs during anion exchange.

In an operating electrochemical cell, a counter electrode reaction occurs simultaneously and in the case of cation electrochemical ion exchange this involves the production of hydrogen ions thereby decreasing the pH of the external solution. These ions will be absorbed as an interfering ion slowly deactivating the electrochemically activated site by recombination.

The electrochemical ion exchange cell can be operated in either batch or continuous flow modes. It is possible by recycling the effluent from a continuous system to operate it in a batch mode.

This modified polymeric elastomer could also form the separating portion of an electrochemical cell or redox cell for energy storage batteries. The membrane for such a cell should have low resistivity, high selectivity, and good chemical resistance for example to an oxidative vanadium electrolyte.

Similarly, those skilled in membrane technology will understand that this process can enable the production of an improved membrane. It will also be understood that in the case of a membrane film, two or more, different polymers may be laminated together to provide films with physical or chemical properties of a more specific nature.

**EXAMPLES.**

1. A polymeric membrane or film is produced by reacting 4,4'diphenylmethane diisocyanate (MDI) with one or more difunctional and/or trifunctional polyhydroxyl containing polyols such that both propylene oxide and ethylene oxide moieties are included in the polymer structure. Suitable catalysts such as stannous octoate together with one or more tertiary amines, in particular, DABCO are provided to control the chemical reaction. Additional crosslinking of the film is achieved by the addition of 1,4-butane diamine. Thus, a polyurethane resin with hydrophilic properties as the continuous phase is obtained. One or more interpenetrating or semi-interpenetrating polymers capable of providing electrical

conductivity and/or ion exchange properties or capable of chemical modification to provide ion exchange properties are included in the polymer matrix. This film or membrane is then further modified by the inclusion of a polymer into the film as previously described so that the polymer now exhibits ionic conductivity, electrical conductivity, or both ionic and electrical conductivity. Typically, polypyrrole will provide electrical conductivity and polystyrene-divinyl benzene resin containing carboxylate groups the ion exchange property. Carbon, metal, metal salts or metal oxides all in a finely divided state may be included into the polyurethane matrix and the polymeric film may additionally contain carbon fibres, metal coated carbon fibres, or metallic threads or wires any or all of which are incorporated into the polymer film either as a woven matt, a continuous fibre, or as a chopped strand matt.

2. A polyurethane polymer interpenetrated with polyacrylonitrile groups may be chemically modified by the reaction of the nitrile group present with hydrogen sulphide or a sodium sulphide solution. This reaction may be conveniently conducted by reaction of the polymer with a 10% solution of sodium sulphide for 6 hours at 75°C. The amine group so formed may be further combined with sultones or lactones to produce a polymer with reactive sulphonic or carboxylic acid groups and thereby introducing ionic conductivity into the polymer.

CLAIM.

The claims defining the invention are as follows:

1. A polymeric membrane or film produced from a polyurethane resin containing both poly(propylene oxide) and poly(ethylene oxide) units as the continuous phase and containing one or more interpenetrating or semi-interpenetrating polymers with electrical conductivity and/or ion exchange properties or capable of chemical modification to provide electrical conductivity or ion exchange properties such that the final film or membrane exhibits ionic conductivity, electrical conductivity, or both ionic and electrical conductivity.
2. A polymeric membrane or film as described in Claim 1 and additionally containing one or more of the following materials in a finely divided state, carbon, metallic powders, metal salts, metal oxides.
3. A polymeric membrane or film as described in Claim 1 or Claim 2 and additionally containing carbon fibres, metal coated carbon fibres, metallic threads, wires, or a combination of both any or all of which are incorporated into the membrane or film as a woven matt, continuous fibres or as a chopped strand matt.

WILLIAM HAROLD JAY.  
1 JULY, 1992.

AUSTRALIA

Patents Act 1990

## PATENT REQUEST: PETTY PATENT

I / We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying Petty complete specification.  
Full application details follow.

[71] Applicant	WILLIAM HAROLD JAY		
Address	64 TURANA ST DONCASTER 3108		
[73] Nominated Person	WILLIAM HAROLD JAY		
Address	64 TURANA ST DONCASTER 3108		
[54] Invention Title	AN IMPROVED ELECTROCHEMICAL MEMBRANE FILM OR FIBRE		
[72] Name(s) of actual inventor(s)	WILLIAM HAROLD JAY		
[74] Address for service in Australia	64 TURANA ST DONCASTER 3108		
	Attorney Code _____		

## BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
.....			
.....			
.....			

## DIVISIONAL APPLICATION DETAILS

[62] Original application number	W. 621 010792
Person by whom made	

William Jay  
(Signature of Applicant)

1 July 1992  
(Date)

\* Delete as appropriate

AUSTRALIA

Patents Act 1990

## NOTICE OF ENTITLEMENT

(To be filed before acceptance)

I, WILLIAMS HAROLD JAY  
of 64 TRAMPS ST DONCASTER 3108

being the applicant in respect of Application No. ...., state the following:-

Part 1 - Must be completed for all applications.

The person(s) nominated for the grant of the patent:

WILLIAMS HAROLD JAY

\*is / \*are the actual inventor(s)

or

\*has entitlement from the actual inventor(s).....

(eg by assignment, by mesne assignment, as legal representative of ...., etc)

Part 2 - Must be completed if the application is associated with one or more provisional applications.

The person (s) nominated for the grant of the patent:

\*is / \*are the applicant(s) of the provisional application(s) listed on the patent request form

or

has entitlement to make a request under Section 113 in relation to the provisional application(s) listed on the patent request form .....

(eg by assignment, by agreement, etc)

Part 3 - Must be completed for all conversion applications.

The person(s) nominated for the grant of the patent:

\*is / \*are the applicant(s) of the basic application(s) listed on the patent request form

or

\*has entitlement from the applicant(s) of the basic application(s) listed on the patent request form .....

(eg by assignment, by mesne assignment, by consent, etc)

(Continued over)

\* Part 6 - Must be completed if the application relates to a microorganism and relies on Section 6 of the Act.

The person(s) nominated for the grant of the patent:

\* is / \*are the depositor(s) of the deposit(s) as listed hereafter *WILFRED HAROLD WATKINS*

or

\* has entitlement from the depositor(s) of the deposit(s) as listed hereafter .....

(eg by assignment, by consent, etc)

Deposit List (by number, deposit institution, date)

*Wilf Watkins*  
(Signature)

*1 July 1992*  
(Date)

\* Part 7 - Must be completed if the applicant for a patent of addition is not the applicant or patentee of the main invention.

I, .....  
the \*applicant / \*patentee for \*application / \*patent No. ....  
authorise .....

to apply for a further patent for an improvement in, or modification of, the main invention.

Note: This part must be signed by the applicant/patentee of the main invention.

.....  
(Signature)

.....  
(Date)

\* Omit/Delete if not appropriate